

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

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Method Of Forming Integrated Circuitry, Method  
Of Forming Memory Circuitry, And Method Of  
Forming Non-Volatile Random Access Memory  
Circuitry

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ATTORNEY'S DOCKET NO. MI22-1669

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# Method Of Forming Integrated Circuitry, Method Of Forming Memory Circuitry, And Method Of Forming Non-Volatile Random Access Memory Circuitry

## TECHNICAL FIELD

This invention relates to methods of forming integrated circuitry, for example memory integrated circuitry.

## BACKGROUND OF THE INVENTION

Semiconductor fabrication continues to strive to make individual electronic components smaller and smaller, resulting in ever denser integrated circuitry. One type of integrated circuitry comprises memory circuitry where information is stored in the form of binary data. The circuitry can be fabricated such that the data is volatile or non-volatile. Volatile storing memory devices result in loss of data when power is interrupted. Non-volatile memory circuitry retains the stored data even when power is interrupted.

This invention was principally motivated in making improvements to the design and operation of memory circuitry disclosed in the Kozicki et al. U.S. Patent Nos. 5,761,115; 5,896,312; 5,914,893; and 6,084,796, which ultimately resulted from U.S. Patent Application Serial No. 08/652,706, filed on May 30, 1996, disclosing what is referred to as a programmable metallization cell. These patents are hereby incorporated by reference. Such a cell includes opposing electrodes having an insulating dielectric material received therebetween.

Received within the dielectric material is a fast ion conductor material. The resistance of such material can be changed between highly insulative and highly conductive states. In its normal high resistive state, to perform a write operation, a voltage potential is applied to a certain one of the electrodes, with the other of the electrode being held at zero voltage or ground. The electrode having the voltage applied thereto functions as an anode, while the electrode held at zero or ground functions as a cathode. The nature of the fast ion conductor material is such that it undergoes a chemical and structural change at a certain applied voltage. Specifically, at some suitable threshold voltage, plating of metal from metal ions within the material begins to occur on the cathode and grows or progresses through the fast ion conductor toward the other anode electrode. With such voltage continued to be applied, the process continues until a single conductive dendrite or filament extends between the electrodes, effectively metal interconnecting the top and bottom electrodes to electrically short them together.

Once this occurs, dendrite growth stops, and is retained when the voltage potentials are removed. Such can effectively result in the resistance of the mass of fast ion conductor material between electrodes dropping by a factor of 1,000. Such material can be returned to its highly resistive state by reversing the voltage potential between the anode and cathode, whereby the filament disappears. Again, the highly resistive state is maintained once the reverse voltage potentials are removed. Accordingly, such a device can, for example, function as a programmable memory cell of memory circuitry.

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The preferred resistance variable material received between the electrodes typically and preferably comprises a chalcogenide material having metal ions diffused therein. A specific example is germanium selenide having silver ions diffused therein. The present method of providing the silver ions within the germanium selenide material is to initially chemical vapor deposit the germanium selenide glass without any silver being received therein. A thin layer of silver is thereafter deposited upon the glass, for example by sputtering, physical vapor deposition or other technique. An exemplary thickness is 200 Angstroms or less. The layer of silver is irradiated, preferably with electromagnetic energy at a wavelength less than 500 nanometers. The thin nature of the deposited silver enables such energy to pass through the silver to the silver/glass interface effective to break a chalcogenide bond of the chalcogenide material. This may form  $\text{Ag}_2\text{Se}$ , which diffuses into the germanium selenide glass and effectively dopes the glass with silver. The applied energy and overlying silver ultimately result in the silver migrating into the glass layer such that a typical homogenous distribution of silver throughout the layer is achieved.

Saturation of silver in germanium selenide is apparently at about 35 atomic percent. Yet, preferred existing technology for cell fabrication constitutes a concentration which is less than 35%, for example 27%.

After the chalcogenide material is provided with silver to a desired concentration, the top electrode material (typically silver) is next deposited. Subsequently, insulating dielectric layers, such as doped glasses and interlevel dielectric layers are deposited, as are conductive metal interconnect layers.

Formation of the conductive metal layers after formation of chalcogenide device components typically results in the substrate being exposed to high temperatures. Unfortunately, this can adversely effect properties of the chalcogenide devices.

It would be desirable to overcome or at least reduce this problem. While the invention was principally motivated in overcoming this problem, it is in no way so limited. The artisan will appreciate applicability of the invention in other aspects unrelated to the problem, with the invention only being limited by the accompanying claims as literally worded and as appropriately interpreted in accordance with the doctrine of equivalents.

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## SUMMARY

The invention includes methods of forming integrated circuitry, methods of forming memory circuitry, and methods of forming non-volatile random access memory circuitry. In one implementation, a method of forming memory circuitry sequentially includes forming a plurality of metal interconnect lines over a semiconductive substrate. A plurality of memory cell storage devices comprising voltage or current controlled resistance setable semiconductive material are then formed. In one implementation, a method of forming integrated circuitry includes forming a metal interconnect line over a semiconductive substrate. A device comprising two metal comprising electrodes separated by a voltage or current controlled resistance setable semiconductive material is formed. The resistance setable semiconductive material is formed after forming the metal interconnect line.

Other implementations and aspects are contemplated and disclosed.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic sectional view of a semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 2 is a view of the Fig. 1 wafer fragment at a processing step subsequent to that shown by Fig. 1.

Fig. 3 is a diagrammatic sectional view of an alternate embodiment semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 4 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that shown by Fig. 3.

Fig. 5 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that shown by Fig. 4.

Fig. 6 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that shown by Fig. 5.

Fig. 7 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that shown by Fig. 6.

Fig. 8 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that shown by Fig. 7.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

Referring to Fig. 1, a semiconductor wafer fragment 10 comprises a bulk monocrystalline semiconductive substrate 12 and is shown in but one preferred embodiment of a method of forming integrated circuitry, for example integrated circuitry comprising voltage or current controlled resistance setable material. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above. Also in the context of this document, the term "layer" encompasses both the singular and the plural unless otherwise indicated. Further, it will be appreciated by the artisan that "resistance setable material" includes material wherein a property or properties in addition to resistance is/are also varied. For example, and by way of example only, the material's capacitance and/or inductance might also be changed in addition to resistance.

Fig. 1 depicts but one preferred implementation of the invention in a method of forming non-volatile random access memory circuitry. A plurality of

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memory cell access transistor gates 14, 16, 18 and 20 are formed over semiconductor substrate 12. By way of example only, such comprise a gate dielectric layer 22, an overlying conductively doped polysilicon layer 24, an overlying conductive metal silicide layer 26, an insulative cap 28, and opposing anisotropically etched insulative sidewall spacers 30. In the depicted preferred embodiment, gate constructions 14-20 are in the form of memory cell wordlines. Substrate isolation, for example LOCOS field isolation oxide or trench isolation, is not shown for clarity, and as not constituting particular materiality to the invention. Discussion proceeds with processing particularly material to memory cell wordlines 16 and 18 which are proximate one another.

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A planarized insulating layer 30 has been formed over the illustrated transistor gates and substrate 12. An example preferred material is borophosphosilicate glass (BPSG) deposited by chemical vapor deposition and planarized back by a polishing, for example chemical-mechanical polishing. Contact openings 32 have been formed therein to semiconductor substrate 12 and filled with a conductive plugging material 34. An example material for plugging material 34 is conductively doped polysilicon. Of course, conductive metal or metal compound layers might also be formed to constitute some or all of material 34.

Another insulative material layer 36 has been deposited and planarized. Again, BPSG is but one exemplary material for layer 36. In one embodiment, at least one of materials 30 and 36 comprises a boron and/or phosphorus doped silicon dioxide glass comprising layer. Such can also be planarized or

otherwise processed by reflow at a temperature of at least 750°C. A contact opening 38 has been formed therethrough to the conductive plugging material 34 which is received between memory cell wordlines 16 and 18. Such has been filled with a conductive plugging material 40. Exemplary materials for material 40 include conductively doped semiconductive materials, such as polysilicon, and metal or metal compounds, and mixtures thereof. At least one metal bit line 42 is formed in electrical connection with material 40 as shown. Thereby in this but one exemplary embodiment, bit line 42 is formed in electrical connection with the active area of semiconductive substrate 12 located between memory cell wordlines 16 and 18. In the context of this document, "metal bit line" defines a conductive bit line which includes at least one of, a) a conductive metal in elemental form; b) a conductive metal alloy comprising at least two elemental metals; and c) a conductive metal compound other than a silicide. By way of example only, exemplary elemental metals and alloys thereof include aluminum, copper, gold, silver, platinum, palladium and rhodium. By way of example only, exemplary metal compounds include titanium nitride and conductive metal oxides, such as rhodium oxides. In accordance with typical or yet-to-be-developed processing, multiple bit lines 42 would typically be fabricated, with only one such bit line 42 being shown in the depicted cross-section. In one embodiment, such constitutes the first metal layer formed over the substrate and, in some instances, is referred to as the Metal 1 layer by people of skill in the art.

In one considered implementation, metal bit line 42 constitutes a metal interconnect line which is formed over the substrate and memory cell access transistor gates. In the context of this document, "metal interconnect line" defines at least one conductive line which is not a transistor gate line and which electrically connects at least two devices and includes at least one of, a) a conductive metal in element form; b) a conductive metal alloy comprising at least two elemental metals; and c) a conductive metal compound other than a silicide. Of course, interconnect lines 42 might also comprise a conductive metal silicide portion in addition to at least one of the materials referred to above. Examples include titanium silicides and tungsten silicides. Further, interconnect lines 42 might include any combination or mixtures of conductive elemental metals, metal alloys comprising at least two elemental metals, at least one conductive metal compound other than a silicide, and a conductive metal silicide. Further, the metal interconnect lines might consist essentially of any of these materials, alone or in combination.

Referring to Fig. 2, an interlevel dielectric layer 44 is formed over dielectric layer 36 and metal interconnect lines/bit lines 42. Exemplary materials include undoped silicon dioxide and silicon nitride. Container openings 46 are etched into insulating materials 44 and 36 to the conductive plugging material 34 which is received on respective lateral outer sides of wordlines 16 and 18. Respective first memory cell electrodes 48 are formed within container openings 46 and, accordingly, in electrical connection with active area of semiconductive substrate 12 on respective lateral outer sides of wordlines 16

and 18. Accordingly, the exemplary respective first memory cell electrodes are formed in electrical connection with respective memory cell access transistors incorporating the illustrated memory cell access transistor gates. Source/drain regions (not shown) would be provided within or proximate semiconductive substrate 12. Exemplary preferred materials for first electrodes 48 include elemental metals, metal alloys and conductive metal compounds. Exemplary preferred materials include silver, for example silver in elemental or alloy form. Such material would preferably be deposited by physical or chemical vapor deposition, planarize polished back, and then recess etched to slightly below the outermost surface of interlevel dielectric layer 44, as shown.

A voltage or current controlled resistance setable semiconductive material 50 is formed in electrical connection with the respective first electrodes 48. Exemplary resistance setable semiconductive material includes chalcogenide material having metal ions diffused therein. One exemplary material comprises  $Ge_xA_y$ , where "A" is selected from the group consisting of Se, Te, S, and mixtures thereof. Exemplary preferred metal ions within material 50 include silver ions. An example preferred method for forming material 50 is by chemical vapor deposition followed by a thin metal layer deposition thereon (i.e., preferably to less than 30% of the thickness of material 50). Exemplary preferred materials for the metal include silver and copper. Such metal is then preferably irradiated effective to break a chalcogenide bond of the chalcogenide material at an interface of such metal and chalcogenide material, and diffuse at least some of the metal into the

chalcogenide material to diffuse metal ions therein. A preferred irradiating includes exposure to actinic radiation having a wavelength of from about 164-904 nanometers, with radiation exposure at between 404-408 nanometers being a more specific example. An even more specific example is a flood UV exposure tool operating at 4.5 milliwatts/cm<sup>2</sup> energy for 15 minutes in an oxygen-containing ambient at room temperature and pressure. The thickness of the metal layer is also preferably chosen to be suitably thin to enable the impinging electromagnetic radiation to essentially transparently pass through such metal to the interface of such metal with the chalcogenide material. Such layer is ultimately preferably planarized and recess etched back slightly relative to interlevel dielectric layer 44, as shown.

At least one second memory cell electrode 52 is formed in electrical connection with voltage or current controlled resistance settable material 50. In the preferred embodiments, such results in the formation of the depicted at least two non-volatile random access memory cells 54 and 56. In such depicted preferred embodiments, second memory cell electrode 52 is common to each of memory cells 54 and 56, and preferably common to other memory cells which are formed. Further in one preferred and the depicted preferred embodiment, first memory cell electrodes, the resistance settable semiconductive material, and the second memory cell electrode(s) are formed into respective memory cell container shapes. Further preferably in one embodiment, the metal ions received within chalcogenide material 50 include silver, and preferably at

least one of the first and second electrodes comprises silver and more preferably silver in elemental form.

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Such provides but a few examples of forming integrated circuitry, such as memory circuitry in accordance with but some aspects of the invention, with memory cells 54 and 56 constituting but exemplary memory cell storage devices comprising voltage or current controlled resistance setable semiconductive material. Yet in one aspect, the invention comprises a method of forming any memory circuitry which sequentially comprises the formation of some plurality of metal interconnect lines over a semiconductive substrate followed by the formation of a plurality of memory cell storage devices comprising voltage or current controlled resistance setable semiconductive material. Further considered, the invention comprises any method of forming integrated circuitry (whether existing or yet-to-be-developed) which sequentially comprises forming at least one metal interconnect line over a semiconductive substrate followed by the formation of any device comprising two metal comprising electrodes separated by a voltage or current controlled resistance setable semiconductive material.

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These and other aspects of the invention are also considered and contemplated by way of example only with respect to but one exemplary alternate embodiment depicted in Figs. 3-8. Fig. 3 depicts a wafer fragment 60 comprising a bulk semiconductive substrate 62 having an exemplary shallow trench field isolation region 64 formed therein. Various exemplary conductive device components 66, 68, 70, 72, 74 and 76 are shown as being formed over substrate 62. Such might constitute completed devices or devices in fabrication

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in the form of conductive lines, such as interconnect lines or field effect transistor lines, or any other conductive device or component thereof. By way of illustration and example only, such device components are depicted as having conductive polysilicon portions 77, overlying metal portions 79, and insulative silicon nitride caps 78. A dielectric layer 80 has been deposited, and planarized back. An exemplary silicon nitride layer 82 is formed thereover. Exemplary contact openings have been formed through layers 82 and 78 with respect to conductive device component 66, 68, 70, 74 and 76.

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Referring to Fig. 4, a conductive layer is deposited and patterned to form at least one metal interconnect line 84 over the illustrated two conductive device components 70 and 72. Such is preferably formed by suitable metal, metals, or metal compound(s) deposition/formation, followed by photolithographic patterning and etch. Exemplary materials for the subject metal layer include tungsten nitride, tungsten, nickel, copper and mixtures thereof. Such provides but one example of forming a metal interconnect line over two conductive device components in the context of but one aspect of the invention.

Referring to Fig. 5, at least one opening 82 is formed through metal interconnect line 84 to at least one of the two conductive device components, with only a single opening 82 being shown formed to conductive device component 72. Preferred methods by which opening 82 is formed include photolithography and etching of metal interconnect line 80.

Referring to Fig. 6 a preferred chalcogenide comprising material 85 is deposited as shown. Such material is patterned, polished or etched

back (Fig. 7) by wet or dry processes. Metal ion insertion/doping thereof is preferably conducted as part of the Fig. 6 processing or as part of the Fig. 7 processing, and is preferably conducted by way of example only by metal layer irradiation as described above. Regardless, such provides but one example of forming voltage or current controlled resistance setable semiconductive material 85 within opening 82 in electrical connection with the respective one of the exemplary subject two device components 70 and 72, with the depicted example showing such material being formed to only partially fill opening 82.

Referring to Fig. 8, a conductive material 88 is formed within opening 82 in electrical connection with resistance setable semiconductive material 85 and in electrical connection with metal interconnect line 84. Preferably in connection with the above-described preferred embodiments, at least one of the conductive material 88 and that of device component 72 comprises silver, and more preferably elemental silver. Any other alternate conductive material, whether existing or yet-to-be-developed, is also contemplated, of course. As shown in one preferred embodiment, conductive material 88 is formed to less than completely fill remaining portions of opening 82, with a preferred container shape being formed as shown in Fig. 8.

Such provides but one example of forming voltage or current controlled resistance setable semiconductive material 84 within opening 82 in electrical connection with the respective one of the two device components and in electrical connection with metal interconnect line 84 with, in the depicted



preferred embodiment, such being provided by the provision of a conductive material 88.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

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